A MODEL FOR THE CHARGE/DISCHARGE PROCESS OF MANGANESE OXIDE THIN FILMS

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Electrolytic manganese dioxide is well known as an excellent electrode material and is the most suitable form of manganese dioxide as active material in alkaline cells. The main problem limiting the rechargeability is caused by irreversible structural changes accompanying the oxidation/reduction process in aqueous solutions leading to the formation of electrochemical inactive compounds. The in situ optical characterization of MnO_2 films is very valuable to correlate the charge storage capacity as well as the structural changes as a function of the applied potential.

In this work the ellipsometric behaviour of thin films of manganese oxide is studied. Manganese oxide films of different thicknesses were deposited on a platinum substrate from 0.1M $MnSO_4$ + 0.017M H_2SO_4 (pH 2) solutions by applying potentiostatic pulses. The ellipsometric characterization of the anodic film growth was performed in the deposition solution while the optical response during successive charge/discharge cycles at 5 mV s^{-1} was studied in alkaline borate solutions (pH 9.2). Ellipsometric measurements were made in a Rudolph Research 2000 FT rotating analyzer automatic ellipsometer. The wavelength employed was 546.1 nm with the incident light beam at 70º.

Although the Ψ - Δ response for the growth can be fitted in the whole thickness range by means of a single film model with optical anisotropy of the oxide, the diferences obtained with an isotropic single film model appear at thicknesses higher than 150 nm. Thus, the isotropic model was chosen for analysing the optical properties and to calculate the thickness of manganese oxide thin films (up to *ca.* 150 nm).

The ellipsometric results for films of different thicknesses electroreduced at -0.5V show changes in the optical constants as compared with those of oxidized samples leading to a decrese of both, the refractive index and the extinction coefficient. Also, the calculated thickness show an overall increase of about 12% on electroreduction.

The optical response for thin films (*ca.* 20 nm) is highly reversible during successive charge/discharge cycles while for thicker films (*ca.* 100 nm) a pronounced irreversibility is observed. The optical data were analysed in terms of two-layer models with an interface sweeping inward from the electrolytic interface or outward from the substrate interface or a one-layer model with the refractive index of a homogeneous film varying continuously during the conversion process.

The ellipsometric behaviour during cycling can be correlated with the potendiodynamic results. A slight decrease of the anodic and cathodic charges associated with the Mn(IV)/Mn(III) redox couple with cycling is obtained for thin films while the diminution is more pronounced for thicker films. This loss of charge can be associtated with the formation of inactive species of Mn(III) which accumulate during cycling.

The Ψ - Δ response for the electroreduction of films of low or intermediate thickness (10 to 100 nm) is consistent with a conversion process of MnO_2 to MnOOH in which the thickness of an outer layer of MnOOH increases gradually at the expense of the MnO_2 innner layer.

The optical hysteresis obtained during reduction/oxydation cycles can be explained trough a model which takes into account the formation of inactive species (loss of charge during cycling) and a continuous increase of thickness during cycling which can be associated to ions and molecules exchange (H^+ and OH^- groups, H_2O molecules) between the lattice and the electrolytic solution.

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